

emission from the fluorophore molecules, which are excited by evanescent waves penetrating shallowly beyond the fiber surface 22, enters the fiber 21 and is detected at the entrance end of the fiber 21 by a monochromator-detector 24 which utilizes an objective 24' and mirror 24" configuration to direct the fluorescence emission (shown by arrows B). Detection at the distal end of the fiber 21 is also possible as is known to those of ordinary skill in the art. Evanescent-wave excitation of fluorophore molecules provides distributed sensing so that the optical fiber probe 20 may provide a spatial profile of the measurand along the length of the fiber, which is sandwiched between layers of cloth prepreggated with a resin or placed within a preformed fibrous structure.

The fluorophores of the invention are especially useful when a probe configuration based on evanescent-wave induced fluorescence spectroscopy is used for cure monitoring. This is due to the fact that the fluorophores of the invention absorb visible light from the Argon ion laser, which is typically utilized in this configuration. As an example, DANS, ANEPPS, AHPBS, ABPBS, and DHASP-PS were each used to monitor the cure, at 60° C. for 100 minutes, of an epoxy resin that was a stoichiometric mixture of DGEBA and PACM. The wavelengths of light from an Argon ion laser for exciting DANS, ANEPPS, AHPBS, ABPBS, and DHASP-PS are 454 nm, 497 nm, 514 nm, 514 nm, and 488 nm, respectively. The values of the overall decrease in the peak fluorescence wavelength for DANS, ANEPPS, AHPBS, ABPBS, and DHASP-PS were 69 nm, 61 nm, 55 nm, 44 nm, and 37 nm, respectively. After the post-cure of 16 hours at 130° C., the values of the overall decrease (compared to the uncured resin) in the peak fluorescence wavelength for DANS, ANEPPS, AHPBS, ABPBS, and DHASP-PS were 89 nm, 68 nm, 62 nm, 50 nm, and 43 nm, respectively.

Although a wavelength-shift fluorophore is added to the polymerizing (or thermoplastic) material at very low concentrations (10 to 100 ppm by weight), the addition of a fluorophore is not practical in some cases, for example, when it discolors the products or when it is required in an excessive amount for large-sized products. In such cases, the fluorophore may be immobilized by covalent bonding on the surface 15 of the optic fiber probe's window 13 that is in contact with the polymerizing (or thermoplastic) material (FIG. 2) or, when evanescent-wave excitation is used, immobilized on the surface 22 of the uncoated optic fiber 21 (FIG. 3). For example, the glass or alumina surface 15 of the window 13 or the surface 22 of the uncoated optic fiber 21 is first modified by reaction with omega-isocyanatoalkyltriethoxysilane. The fluorophore 4-(N-hydroxymethyl-N-methylamino)-4'-nitrostilbene is then immobilized on the modified surface by reaction with the isocyanato group. Finally, the surface 15, 22 with the immobilized fluorophore molecules is conditioned before the use of the optic fiber probe 10, 20 by immersing the modified optic fiber 21 in the material 25 to be monitored or by coating the modified window surface 15 with a thin layer of the material to be monitored.

In one example of immobilization of a fluorophore by covalent bonding, glass fiber was silanized with the use of 3-aminopropyltriethoxy silane. A dansyl fluorophore was then covalently immobilized on the silanized glass fiber by the reaction of the silanized glass with 5-dimethylamino-1-sulfonyl chloride ("dansyl chloride"). The overall decrease in the peak fluorescence wavelength of the immobilized dansyl fluorophore during the cure of a stoichiometric mixture of DGEBA and PACM at 100° C. for one hour was

75 nm, indicating that the dansyl fluorophore was effective for cure monitoring of the epoxy resin even when it was covalently immobilized.

Alternatively, the fluorophore is immobilized by physical adsorption on the surface 15 of the optic fiber probe's window 13 that is in contact with the polymerizing (or thermoplastic) material or, when evanescent-wave excitation is used, on the surface 22 of the uncoated optic fiber 21. When it is desirable to increase the fluorescence intensity to facilitate the determination of the fluorescence peak, the number of the fluorophore molecules that are immobilized on the surface 15, 22 is increased by increasing the surface area of the window surface 15 or the surface 22 of the uncoated optic fiber 21. This is accomplished, for example, by coating the surface 15 or the uncoated optic fiber 21 with porous sol-gel glass, by attaching porous particles on the surface 15, 22 with a binder, or by attaching or fastening a thin, clear, porous disk on the surface 15 of the window that is in contact with the material being monitored. Finally, the surface 15, 22 with the immobilized fluorophore molecules is conditioned before the use of the optic fiber probe 10 or 20 by immersing the modified optic fiber 21 in the material to be monitored or by coating the modified window surface 15 with a thin layer of the material to be monitored.

In one example of immobilization of a fluorophore by physical adsorption, DHASP-PS was immobilized on a porous silica surface by adsorption. During the cure of a stoichiometric mixture of DGEBA and PACM at 60° C. for 1.75 hours, the peak fluorescence wavelength of the immobilized DHASP-PS fluorophore decreased from 590 nm to 565 nm, with a decrease of 25 nm, while the peak fluorescence wavelength of the same fluorophore dissolved in the same epoxy resin decreased from 593 to 555 nm, with a decrease of 38 nm. Thus, even when the DHASP-PS fluorophore was immobilized by physical adsorption, it was effective for cure monitoring of the epoxy resin.

Although the invention has been described in considerable detail with respect to preferred embodiments thereof, variations and modifications will be apparent to those skilled in the art without departing from the spirit and scope of the invention as set forth in the claims. Moreover, although the present disclosure focuses primarily on monitoring the extent of cure of a polymerizing material, it is to be understood that the method of the invention and class of fluorophores described herein are equally useful in connection with monitoring the extent of solidification of a thermoplastic polymer.

We claim:

1. A method of measuring extent of cure of a polymerizing material comprising the steps of:
 - selecting a polymerizing material;
 - selecting a wavelength-shift fluorophore;
 - dissolving said fluorophore in said polymerizing material;
 - measuring change in peak fluorescence wavelength of said fluorophore resulting from a change in polarity and mobility of the polymerizing material surrounding said fluorophore; and
 - comparing said change with a known value to determine extent of cure of said polymerizing material.
2. The method according to claim 1 further comprising the step of attaching at least one moiety to said fluorophore before said step of dissolving, said moiety being selected from the group of reactive moieties of said polymerizing material.
3. The method according to claim 2 wherein said polymerizing material comprises methacrylate or methacrylic